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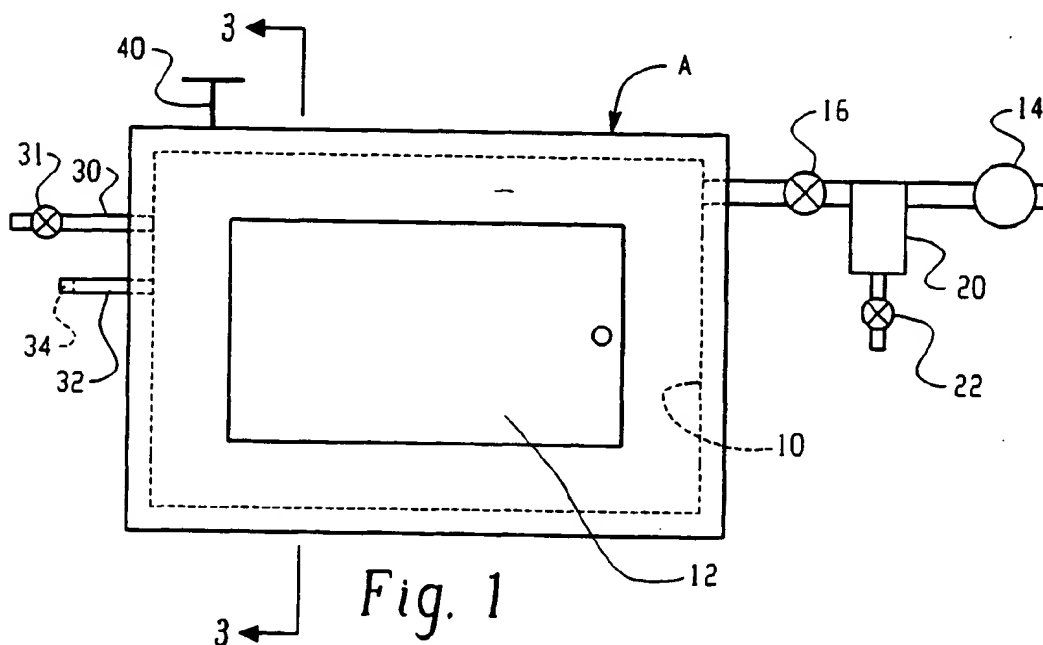
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(54) Method for modifying surfaces with ultra thin films

(57) A substrate surface is coated with a thin film by exposing the substrate to a vapor of amphiphilic mole-

cules in a vacuum chamber (A), and allowing the amphiphilic molecules to spontaneously self-assemble and attach to the substrate surface.



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Description

BACKGROUND OF THE INVENTION

[0001] This application relates to the art of ultra thin films and, more particularly, to such films that are formed of amphiphilic molecules. The invention is particularly applicable to a method of applying such films to substrate surfaces and will be described with specific reference thereto. However, it will be appreciated that certain features of the invention have broader aspects, and may be used in other methods as well as for other purposes.

[0002] Polymerizable amphiphilic molecules having the intrinsic ability to self-assemble in a thin film are well known. By way of example, descriptions of such materials and their ability to form thin films are contained in: W.C. Bigelow et al, *J. Colloid. Sci.*, 1, 513-538 (1946); L.H. Lee, *J. Colloid. & Interface Sci.*, 27, 751-760 (1968); E.E. Polymeropoulos et al, *J. Chem. Phys.*, 69, 1836-1847 (1978); and J. Sagiv, U.S. Patent No. 4,539,061, issued September 3, 1985. The disclosures of which are hereby incorporated herein by reference. These publications disclose compositions that include solvents in which a film forming substance is soluble, and the solvents usually are toxic and environmentally unfriendly. Highly liquid compositions also lose their usefulness very rapidly when exposed to airborne moisture because the amphiphilic molecules are highly reactive with water and tend to form molecular agglomerations that precipitate out of the solution.

[0003] Compositions and methods for use in applying ultra thin films of self-assembling amphiphilic molecules to substrate surfaces are described in our commonly assigned U.S. patent Nos. 5,078,791; 5,106,561; 5,166,000; 5,173,365; 5,204,126; 5,219,654 and 5,300,561, the disclosures of which are hereby incorporated herein by reference. These compositions and methods are advantageous for providing ultra thin films on porous and non-porous surfaces of such materials as glass, ceramic, porcelain, fiber glass, metals and plastics. The film serves one or more of a variety of purposes including scratch resistance, corrosion protection, protection for anti-reflective coatings on lenses, friction reduction, print priming, moisture barriers, and the like. For example, the films may be used for coating laboratory glassware and for providing a non-stick coating for pots, pans, dishes or utensils. These films are particularly advantageous for use on anti-reflective glass and plastic lens surfaces, including plastic eyewear lenses manufactured from CR-39 (trademark of PPG Industries), polycarbonate and high index resins that are pre-treated with a hard coat for scratch resistance.

[0004] The gas phase reaction of different amphiphilic organosilanes with a silica surface in vacuum cell has been reported by a number of authors: *J. Phys. Chem.* 70, 2937 (1966); *Trans. Faraday Soc.*, 63, 2549 (1967); *J. Phys. Chem.*, 73, 2372 (1969); *Langmuir*, 7, 923

(1991). The disclosures of which are hereby incorporated herein by reference. Commercial hydrophobic fumed silicas such as Aerosil R 972 from Degussa Corp. and Cab-O-Sil TT-610 from Cabot Corp. are produced using dichlorodimethylsilane by gas phase reactions. Recently, others have also reported the formation of hydrophobic silica using other amphiphilic alkylsilanes in a gas phase reaction inside a vacuum cell: *Langmuir*, 9, 3518 (1993); *Langmuir*, 13, 1877 (1997). The disclosures of which are hereby incorporated herein by reference. The reactions reported in these articles were performed to coat silica at very high temperatures in the range of 200-300°C or higher. A lower temperature inside the cell results in the absence of any coating on the silica surface because the molecules used in the process require a high temperature for achieving a thermal reaction. Also, the process requires steam hydration followed by dehydration at a high temperature of 400°C or above along with degassing. The apparatus and the process are limited to preparation of small samples of the coated material because an extremely strong vacuum is required and the vacuum cell is small.

[0005] The use of prior compositions and methods to form a film on a substrate surface leaves excess composition on the surface that must be removed. Disposal of this excess material is difficult, and it is difficult to remove from the excess material from irregular surfaces. Large articles and surfaces with microstructures are difficult to coat when using prior compositions and methods, and the process is very slow. Prior methods require large quantities of coating composition that usually is obtained by repeatedly removing smaller quantities from one open container so that vigilance is necessary to prevent contamination of the composition and exposure to moisture.

[0006] It would be desirable to have a process for applying hydrophobic thin films of amphiphilic molecules to different surfaces in a manner that is very fast and cost effective. It would also be desirable to have a process that could be used to coat substrate surfaces of any size or shape without requiring removal of excess coating composition and disposal of same.

SUMMARY OF THE INVENTION

[0007] In accordance with the present application, thin films of amphiphilic molecules are formed on substrate surfaces by vapor phase coating. Vapor phase reactions are usually clean and very fast, and the need to dispose of excess material or clean the coated surfaces is minimized.

[0008] In accordance with the present application, a vacuum chamber containing substrates to be coated is charged with polymerizable amphiphilic molecules in a gas phase. The amphiphilic molecules spontaneously self-assemble and bond to the substrate surfaces in a substantially continuous thin film by reactions and forces of the type discussed in the aforementioned articles

by Bigelow et al, L.H. Lee, E.E. Polymeropoulos et al, and J. Sagiv. In one arrangement, the vacuum chamber is charged with polymerizable amphiphilic molecules in a gas phase by placing within the vacuum chamber with the substrates to be coated a quantity of the molecules in their liquid or solid state. After a vacuum is established in the chamber, the molecules in their liquid or solid state are heated and vaporized to charge the chamber with molecules in their gas phase.

[0009] In another arrangement, polymerizable amphiphilic molecules are converted to their gas phase externally of the vacuum chamber and introduced into the chamber after a vacuum has been established therein.

[0010] The gas phase molecules spontaneously spread uniformly throughout the vacuum chamber and come into contact with the substrate surfaces to self-assemble thereon and bond thereto in a substantially continuous film of substantially uniform thickness.

[0011] The vacuum that is established in the vacuum chamber is between 2×10^{-2} torr (2.666×10^4 Pa) and 5×10^{-4} torr (0.06665 Pa). The principal requirement for the vacuum is that it should be sufficient to promote spontaneous uniform dispersal of the gas phase molecules throughout the chamber when the gas phase molecules are introduced into the chamber either from outside the chamber or by vaporization inside the chamber.

[0012] The temperature of the vacuum chamber preferably is between 20°C and 100°C, and most preferably between 30°C and 50°C. If the temperature is too low, the gas phase amphiphilic molecules will not be sufficiently active for good uniform dispersal throughout the chamber and contact with substrate surfaces. If the temperature is too high, the gas phase amphiphilic molecules will be too active to self-assemble on substrate surfaces.

[0013] The temperature of the vacuum chamber also must be low enough to prevent complete dehydration of the substrate surfaces. Although the substrate surfaces appear visibly dry and are completely dry to the touch, they contain residual traces of airborne moisture that reacts with the amphiphilic molecules to produce the chemical bond between the molecules and the substrate surfaces.

[0014] Very small quantities of liquid or solid polymerizable amphiphilic molecules are used to charge the vacuum chamber with gas phase amphiphilic molecules. The amount of liquid or solid polymerizable amphiphilic molecule material that is used is between $(1-100) \times 10^{-2}$ mmole per cubic foot of vacuum chamber volume. More preferably, the amount is between $(1-30) \times 10^{-2}$ mmole per cubic foot of vacuum chamber volume. Most preferably, the amount is between $(2-10) \times 10^{-2}$ mmole per cubic foot of vacuum chamber volume.

[0015] Thin films that are formed on substrate surfaces in accordance with the present application may have a thickness between 2 and 50 nanometers. Usually, the film will be monomolecular and at the lower end of the thickness range. The thickness may vary depending on

the type and quantity of amphiphilic molecule material used, the temperature of the vacuum chamber, the degree of vacuum and the time that the substrates are left in the vacuum chamber exposed to the gas phase molecules. After the vacuum chamber is charged with polymerizable amphiphilic molecules in the gas phase, substrate surfaces may be exposed to the gas phase molecules for anywhere from 10 seconds to 30 minutes, more preferably 30 seconds to 10 minutes, and most preferably 30 seconds to 5 minutes.

[0016] Following exposure of the substrate surfaces to the gas phase amphiphilic molecules for the desired time to form a continuous thin film, the gas phase molecules are exhausted from the vacuum chamber which is then flooded with air at atmospheric pressure to allow opening of the chamber for removal of the coated substrates and insertion of uncoated ones.

[0017] A variety of different substrate materials can be provided with thin films of amphiphilic molecules in accordance with the method of the present application. Suitable substrate materials include, but are not necessarily limited to, glass, ceramic, porcelain, plastics, anti-reflective coatings on glass or plastic lenses or other surfaces and certain metal surfaces such as silver, gold, silicon, aluminum, germanium, chromium, titanium and zirconium and the like.

[0018] When the gas phase molecules are introduced to the vacuum chamber by vaporization of amphiphilic molecule material within the chamber itself, a frangible or rupturable sealed container of the material, such as a glass ampoule or a DSC cup as shown in the drawing, is placed in the chamber with the substrates to be coated. Following establishment of the vacuum, the container is ruptured and the amphiphilic molecule material is rapidly heated to vaporise same for dispersal throughout the chamber. The sealed rupturable container contains less than 5 grams of amphiphilic molecule material and usually between 0.5 and 5 grams. The sealed rupturable container is purged of air and preferably contains an inert gas such as argon or nitrogen. The free space within the sealed rupturable container that is not occupied by amphiphilic molecule material is at least 90% free of air and more preferably 95 to 100% free of air to avoid exposure of the amphiphilic molecule material to airborne moisture.

[0019] Embodiments of the invention seek to provide one or more of the following advantages, namely:

an improved method for coating substrates with amphiphilic molecules at relatively low temperatures; a method that minimises environmental problems; a method that is energy- and time-efficient; a method that can be used to coat many different substrate materials and shapes; and a method that requires little or no cleaning of the substrate surfaces after it has been coated with a thin film.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020]

Figure 1 is a front elevational view of a conventional vacuum chamber for use in the method of the present invention;

Figure 2 is an elevational view of an external arrangement for vaporising amphiphilic molecule material;

Figure 3 is a cross-sectional elevational view taken generally on line 3-3 of Figure 1;

Figure 4 is an elevational view of a frangible ampoule used in the method of the present application; and

Figure 5 is a cross-sectional elevational view of a Differential Scanning Calorimetry container used in the method of the present application.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0021] As used in the context of this invention, a film forming substance is one containing amphiphilic molecules that are capable of self-assembly, self-polymerization and chemical bonding to chemical groups on the substrate surface or within the surface matrix to form a substantially continuous ultra thin film of substantially uniform thickness. A substantially continuous film is one that is substantially unbroken except for the presence of relatively minor defects or imperfections, such as random and widely scattered pinholes.

[0022] An amphiphile contains a polar region and a non-polar region. Amphiphiles that can be used to form thin films in accordance to the present application include, but are not necessarily limited to, the following:

[0023] The polar segment of the amphiphile can be a carboxylic acid, alcohols, thiols, primary, secondary and tertiary amines, cyanides, silane derivatives and sulfonates and the like.

[0024] The non-polar or apolar component typically consists mainly of alkyl or partial and per fluorinated alkyl groups, alkyl ether or partial and perfluorinated alkyl ether groups. These apolar regions may include diacetylene, vinyl-unsaturated or fused linear or branched aromatic rings.

[0025] In one preferred arrangement, the film forming substance consists essentially of R_mSiX_n where the non-polar R is an alkyl, fluorinated alkyl, alkyl ether or fluorinated alkyl ether of about 1-30 carbons and most preferably about 6-30 carbon atoms. The alkyl chain may contain the diacetylene, vinyl-unsaturated, single aromatic and fused linear or branched aromatic rings. In the above formula X is selected from the group consisting essentially of halogens, hydroxy, alkoxy and acetoxy. In the formula, m is 1-3, n is 1-3 and m+n equal 4. In still another preferred arrangement, R may be a substituted silane or siloxane.

[0026] In another preferred arrangement, the film

forming substance consists essentially of R_mSH_n , where R is an alkyl, fluorinated alkyl, an alkyl ether or a fluorinated alkyl ether, S is sulfur and H is hydrogen. The alkyl chain may contain diacetylene, vinyl, single aromatics, or fused linear or branched aromatic moieties. In the formula, m is 1-2 and n is 0-1.

[0027] In another preferred arrangement, the film forming substance consists essentially of RX, where R is an alkyl, fluorinated alkyl, an alkyl ether or a fluorinated alkyl ether. The alkyl chain may contain diacetylene, vinyl-unsaturated, single aromatic, or fused linear or branched aromatic moieties and, X is selected from the groups of -COOH, -OH and -NH₂.

[0028] Methods for applying ultra thin films of amphiphilic molecules to different substrates having surfaces that are chemically reactive with amphiphilic molecules are described in the articles and the U.S. patents incorporated by reference above. The molecules attach themselves to the substrate surface by various reactions and forces, and are primarily chemically bound to the surface. The molecules self-assemble and self-polymerize on the surface to form the substantially continuous ultra thin film having a substantially uniform thickness.

[0029] The method of the present application allows application of ultra thin films in a very fast and efficient manner to substrates that have irregular surface shapes including shallow engraved profiles or patterns. When these substrates are exposed to the vaporized gas phase amphiphilic molecules inside the vacuum chamber, the amphiphilic molecules self-assemble on the surface of the substrate to form a continuous and uniform thin film.

[0030] A vacuum chamber for use in the method of the present application may be an insulated rectangular metal box having a door which is sealed by a gasket when closed and allows insertion and removal of items. This box has an inside chamber that is attached with a high vacuum pump capable of drawing a vacuum of 10^{-4} torr (0.01333 Pa). The inside chamber is equipped with separate heating devices for heating the chamber and for vaporizing the amphiphilic material. A number of different devices such as resistance electrodes, a resistance heater, an induction coil or an electron beam can be used for rapidly heating the amphiphilic materials to a high temperature for vaporization. A simple electric heater block may be used for this purpose.

[0031] The substrates to be coated with hydrophobic films are placed inside the vacuum chamber. The amphiphilic material either in the sealed ampoule or the DSC cup is also placed in the heating device inside the chamber and the door is closed. A strong vacuum between 2×10^{-2} torr (2.666×10^4 Pa) and 5×10^{-4} torr (0.06665 Pa) quickly is applied to the chamber. The valve connecting the pump to the chamber is closed to keep the chamber at constant high vacuum. The amphiphilic material ampoule is broken open by the device inside the chamber and heated quickly to vaporize the

material. The glass ampoule can also be broken open outside by hand and then put it in the heating device inside the chamber just before closing the door. The gas phase amphiphilic molecules spread uniformly very fast throughout the whole chamber. As the amphiphilic molecule material vaporizes, the vacuum inside the chamber does rise a bit but remains within the range of 2×10^{-2} torr (2.666×10^4 Pa) and 5×10^{-4} torr (0.06665 Pa). The chamber is kept in this condition for a time of 30 sec to 30 min. During this time the amphiphilic molecules self-assemble and attach themselves to the surface of the substrate and form a continuous uniform thin film.

[0032] After the selected time, the vacuum pump valve is opened to evacuate the excess gas phase amphiphilic material from the chamber. A cold trap or condenser between the chamber and the pump condenses and traps the excess amphiphilic material vapor and does not allow it to escape to the atmosphere. Clean air is let into the chamber to bring it up to atmosphere pressure and the chamber is opened to remove the coated substrates.

[0033] The substrates may be coated at chamber temperatures between $20-100^\circ\text{C}$ and more preferably between 30°C and 50°C . The amount of amphiphilic material used may be from $(1-100) \times 10^{-2}$ mmole per cubic foot of chamber volume. A number of different substrates such as glass, ceramic, porcelain, metals, plastics and anti-reflective surfaces are coated with a thin film by the above process.

[0034] As an example, anti-reflective eyeglass lenses are put inside the vacuum chamber. A sealed ampoule containing $(1-100) \times 10^{-2}$ mmole, preferably $(1-30) \times 10^{-2}$ mmole and most preferably $(2-10) \times 10^{-2}$ mmole of the amphiphilic material RmSiXn per cubic foot of the vacuum chamber volume, is put in the heating device and the door is closed. A high vacuum of 2×10^{-2} torr (2.666 Pa) is applied to the chamber. The pump valve is closed to keep the chamber and the lenses at this negative pressure. The ampoule is broken open by the device inside the chamber and the material in the ampoule is heated at $250-350^\circ\text{C}$ for 30 seconds to a minute to completely vaporize it. The chamber is kept under these conditions for another 30 seconds. The vacuum pump valve then is opened and the chamber is evacuated to remove the excess gaseous film forming material. The chamber then is flooded with clean air to bring it to atmospheric pressure and opened for removing the lenses coated with an hydrophobic ultra thin film of amphiphilic molecules.

[0035] In a second example, anti-reflective eyeglass lenses are placed inside the chamber. An ampoule containing the coating material as mentioned above is opened by hand and put in the heating unit inside the chamber. The chamber door is closed and a vacuum of 2×10^{-2} torr (2.666 Pa) is applied. The pump valve is closed and the amphiphilic material is quickly vaporized by heating it at $250-350^\circ\text{C}$. The chamber is kept closed for another 30 seconds followed by evacuation of the

excess gaseous material from the chamber and flooding same with clean air at atmospheric pressure. The chamber then is opened to remove the lenses coated with an hydrophobic ultra thin film of amphiphilic molecules.

[0036] In a third example, anti-reflective eyeglass lenses are put inside the chamber. A DSC cup containing $(2-10) \times 10^{-2}$ mmole of amphiphilic material per cubic foot of chamber volume is placed in the heating device in the chamber. The door is closed and a high vacuum of 2×10^{-2} torr (2.666 Pa) is applied followed by closing of the pump valve to keep the chamber at this pressure. The DSC cup then is heated at $250-350^\circ\text{C}$ for 1-2 minutes to vaporize the material inside the DSC cup. The resulting high pressure within the two part DSC cup causes the parts to separate and the amphiphilic material gas is released into the chamber. The molecules in the vapor phase reach the surface of the lenses and spontaneously self-assemble to form a uniform hydrophobic ultra thin film on them. After 30 seconds to 2 minutes the chamber is evacuated to remove the excess vapor and flooded with clean air at atmospheric pressure. The chamber then is opened to remove the coated lenses.

[0037] In a fourth example, laboratory ware such as round bottom flasks, beakers, Erlenmeyer flasks, and some pipettes are placed inside the chamber along with an ampoule of amphiphilic material in the heating device. After closing the chamber door, a vacuum is applied and the ampoule is broken open and heated to vaporize the amphiphilic material. After 30 seconds to 2 minutes the excess vapor in the chamber is evacuated by the pump and the chamber is flooded with clean air at atmospheric pressure to permit opening of the door. Both inside and outside surfaces of the laboratory ware were coated well with the hydrophobic thin film.

[0038] In a fifth example, glass cookware, dishes and coffee pots were put inside the chamber. An ampoule or a DSC cup containing amphiphilic molecules was placed in the chamber. A vacuum of about 2×10^{-2} torr (2.666 Pa) is established in the chamber and the amphiphilic material is vaporized as described above. After exposure to the vapors for 1-2 minutes the chamber is evacuated and flooded with clean air at atmospheric pressure. The film provides a non-stick coating on the cookware.

[0039] In a sixth example, plastic lenses made of resins such as CR-39 (trademark of PPG, Inc.) polycarbonate, and high index resin with and without scratch resistant coatings were placed inside the chamber at a temperature of 50°C with a DSC cup containing amphiphilic molecules as previously described. After achieving the required vacuum of 2×10^{-2} torr (2.666 Pa), the pump valve is closed and the gas phase amphiphilic material is released in the chamber by heating the DSC cup as described above. The lenses are exposed to the gaseous material for 5-10 minutes followed by evacuation of the vapor and flooding the chamber with clean air at atmospheric pressure. The chamber then is

opened and the lenses removed. All lenses were well coated with the hydrophobic thin film of amphiphilic molecules. Using a glass ampoule containing amphiphilic molecule material in place of the DSC cup gave same results.

[0040] In a seventh example, a few clean silicon wafers were placed inside the chamber with an opened ampoule of amphiphilic material. A vacuum of 2×10^{-2} torr (2.666 Pa) was established in the chamber followed by vaporization of the amphiphilic material. The wafers were treated for one minute followed by evacuation of the vapor and flooding the chamber with air at atmospheric pressure. All wafers were coated very well with the hydrophobic thin film of amphiphilic molecules.

[0041] In an eighth example, substrates like touch-screen, CRT's and photocopy machine top glass plates were coated successfully by the above process.

[0042] In a ninth example, a number of different polished metal surfaces, such as gold and silver, were put in the chamber with an ampoule of amphiphilic material RmSHn. The remaining steps were carried out as described above. After the process, the metal surfaces were coated well with the hydrophobic thin film of amphiphilic molecules.

[0043] Figure 1 shows a vacuum cabinet A having an internal vacuum chamber 10 that can be selectively heated to a desired temperature in a known manner. A door 12 selectively provides access to the interior of chamber 10.

[0044] A vacuum pump 14 is attached with chamber 10 through a valve 16, and a condenser or cold trap 20 which is interposed between chamber 10 and vacuum pump 14. A suitable valved outlet 22 is provided for condenser 20.

[0045] An inlet 30 with a valve 31 may be provided to the interior of vacuum chamber 10. Another conduit attached with chamber 10 is indicated at 32 and has a rubber septum 34 through which a syringe needle may be extended for injecting material to chamber 10. Rubber septum 34 seals itself when the needle is withdrawn.

[0046] A rotatable rod 40 extends through a suitable seal to the interior of chamber 10 and has a laterally extending arm 42 at its bottom end within chamber 10. This rod could be rotated manually or mechanically to rupture the ampoule.

[0047] A stainless steel holder B having a cup 50 and oppositely extending arms 51 and 52 is positioned within chamber 10. Arms 51 and 52 have holes therethrough receiving upright pins 53 and 54 to stabilize holder B. Cup 50 is shown resting on a conventional electric resistance heater 60. It will be recognized that other heating arrangements are also possible. For example, pins 53 and 54 could be electrodes so that stainless steel holder B itself would be a resistance heater. Cup 50 can also be positioned within an induction coil for heating same. A sealed frangible glass ampoule C is closely received within cup 50 and includes a container portion 62 and a frangible portion 64. Rod 40 may be rotated to

engage arm 42 with frangible portion 64 of ampoule C to break same from container portion 62 and expose the contents thereof to chamber 10.

[0048] Figure 2 shows a container 72 in which a small quantity of amphiphilic molecule material is placed. Container 72 is heated by an electrical heater or by a flame to vaporize the amphiphilic molecule material. Vaporization of the material allows the vapors to travel through a glass or metal tube 74 that may be attached to valved inlet 30 for feeding vapor to chamber 10. A syringe needle 76 may be provided on the end of the glass or metal tube 74 for piercing rubber septum 34 to feed gas phase molecules to the interior of chamber 10.

[0049] In operation of the device, door 12 is opened to place substrates to be coated in vacuum chamber 10. Door 12 is then closed and vacuum pump 14 is turned on until the desirable strong vacuum is developed in chamber 10. Valve 16 then is closed to seal chamber 10. Vaporized amphiphilic molecules in their gas phase are then introduced to chamber 10. This may be done by vaporizing amphiphilic molecule material within chamber 10. When that is done, a rupturable container of amphiphilic molecule material is placed within chamber 10 at the same time as the substrates to be coated.

In the alternative, the amphiphilic molecule material may be vaporized externally of chamber 10 and introduced thereto through conduits 30 or 32. After the substrates have been exposed to the gas phase molecules for a desired period of time, usually 30 seconds to 30 minutes, valve 16 is open along with valve 31 and vacuum pump 14 is started to exhaust the excess gas phase amphiphilic molecules which are condensed in condenser 20. Air at atmospheric pressure also flows into chamber 10 so that door 12 can be opened for removing coated articles.

[0050] Figure 4 shows a frangible glass ampoule C having a container portion 62 and a frangible portion 64 that is designed to break at 66. Ampoule 62 is purged of air by flooding it with an inert gas such as argon or nitrogen and a desired quantity, less than 5 grams, of amphiphilic molecule material is placed in container portion C. The end of frangible portion 64 then is sealed as indicated at 68. The free space within ampoule C that is not occupied by the amphiphilic molecule material preferably is at least 90% free of air and more preferably 95-100% free of air. This prevents reaction of the amphiphilic molecule material with any airborne moisture.

[0051] Figure 5 shows a Differential Scanning Calorimetry container D that also is known as a DSC container. The container includes a cup 80 having a circular peripheral wall 82 that terminates in an inwardly inclined portion 84. A cover 86 has a circular peripheral wall 88 that is an interference fit on cup wall 82. An O-ring 90 is positioned between cover 86 and inclined wall 84 for sealing the interior of cup 80. With lid 86 removed, cup 80 is purged of air by flooding same with an inert gas such as argon or nitrogen. A desirable quantity of amphiphilic molecule material, less than 5 grams, then is

placed in cup 80 followed by sealing of cover 86 to cup 80. When DSC cup D is placed in stainless steel holder B and heated, the vapor pressure inside forces cover 86 off from cup 80 to release the vaporized amphiphilic molecules for dispersal in chamber 10. Obviously, other types of sealed rupturable containers may be used for protecting the amphiphilic molecule material until it is desirable to vaporize same to its gas phase for dispersal in vacuum chamber 10.

[0052] Although the invention has been shown and described with respect to preferred embodiments, it is obvious that equivalent alterations and modifications will occur to others skilled in the art upon the reading and understanding of this specification. The present invention includes all such equivalent alterations and modifications, and is limited only by the scope of the claims.

[0053] In view of the foregoing description it will be evident to a person skilled in the art that various modifications may be made within the scope of the invention.

[0054] The scope of the present disclosure includes any novel feature or combination of features disclosed therein either explicitly or implicitly or any generalisation thereof irrespective of whether or not it relates to the claimed invention or mitigates any or all of the problems addressed by the present invention. The applicant hereby gives notice that new claims may be formulated to such features during the prosecution of this application or of any such further application derived therefrom. In particular, with reference to the appended claims, features from dependent claims may be combined with those of the independent claims and features from respective independent claims may be combined in any appropriate manner and not merely in the specific combinations enumerated in the claims.

Claims

1. A method of providing a thin film of amphiphilic molecules on a substrate surface, comprising: exposing the substrate surface to a vapour of amphiphilic molecules in a vacuum at a temperature of less than 100°C.
2. The method of claim 1, including the steps of so exposing the substrate surface for a time that enables the amphiphilic molecules to spontaneously self-assemble and bond to the substrate surface in a substantially continuous thin film.
3. The method of claim 1 or 2, wherein the substrate surface is so exposed by placing the substrate in a chamber, establishing a vacuum in the chamber, and introducing a vapour of amphiphilic molecules into the chamber.
4. The method of claim 3, wherein said step of introducing a vapour is carried out by placing in the chamber with the substrate a quantity of vaporisable film forming material containing amphiphilic molecules, and vaporising the film forming material within the chamber subsequent to the step of establishing a vacuum in the chamber.
5. The method of claim 4, wherein said step of placing a quantity of film forming material in the chamber is carried out by placing a liquid film forming material in the chamber.
6. The method of claim 5 wherein the step of placing a liquid film forming material in the chamber is carried out by breaking open a sealed ampoule containing amphiphilic molecule material and placing same within the chamber immediately prior to establishing a vacuum in the chamber.
7. The method of claim 5 wherein the step of placing a liquid film forming material in the chamber is carried out by placing in the chamber a sealed rupturable container that contains a liquid film forming material.
8. The method of claim 7 wherein said step of placing in the chamber a sealed rupturable container is carried out by placing in the chamber a frangible ampoule that contains a film forming material and further including the step of breaking open the ampoule prior to the step of vaporizing the film forming material.
9. The method of claim 7 wherein said step of placing in the chamber a sealed rupturable container is carried out by placing in the chamber a container having a separable lid sealed thereto, said step of vaporizing being carried out by heating the container to vaporize the film forming material therein and force the lid from the container by action of internal pressure to release the vapor into the chamber.
10. The method of any preceding claim, wherein the step of exposing the substrate surface in a vacuum is carried out at a vacuum between 2×10^{-2} torr (2.666×10^4 Pa) and 5×10^{-4} torr (0.06665 Pa).
11. The method of any preceding claim, wherein the step of exposing the substrate surface to a vapour of amphiphilic molecules in a vacuum is carried out by so exposing the substrate surface for 30 seconds to 30 minutes.
12. The method of any preceding claim, wherein the substrate is so exposed in a vacuum chamber and the amount of film forming material that is vaporised to provide the vapour of amphiphilic molecules is between $(1-100) \times 10^{-2}$ mmole per cubic foot of

chamber volume.

13. The method of any preceding claim, wherein the substrate is so exposed to a vapour of $RmSiX_n$ where R is an alkyl, fluorinated alkyl, alkyl ether or fluorinated alkyl ether of 1-30 carbon atoms, a substituted silane or a siloxane, X is selected from the group consisting essentially of halogens, hydroxy, alkoxy and acetoxy, m is 1-3, n is 1-3 and $m+n=4$. 5
14. The method of any one of claims 1 to 12, wherein the substrate is so exposed to a vapour of $RmSH_n$ where R is an alkyl, fluorinated alkyl, alkyl ether or fluorinated alkyl ether, S is sulphur, H is hydrogen, $m=1-2$ and $n=0-1$. 10 15
15. The method of any one of claims 1 to 12, wherein the substrate is so exposed to a vapour of RX where R is an alkyl, fluorinated alkyl, alkyl ether or fluorinated alkyl ether and X is selected from the groups of $-COOH$, $-OH$ and $-NH_2$. 20
16. A sealed rupturable container containing less than 5 grams by weight of heat vaporisable amphiphilic molecules. 25
17. The container of claim 16, wherein said container comprises a frangible ampoule.
18. The container of claim 16, wherein said container comprises a cup having a separable lid sealed thereto. 30

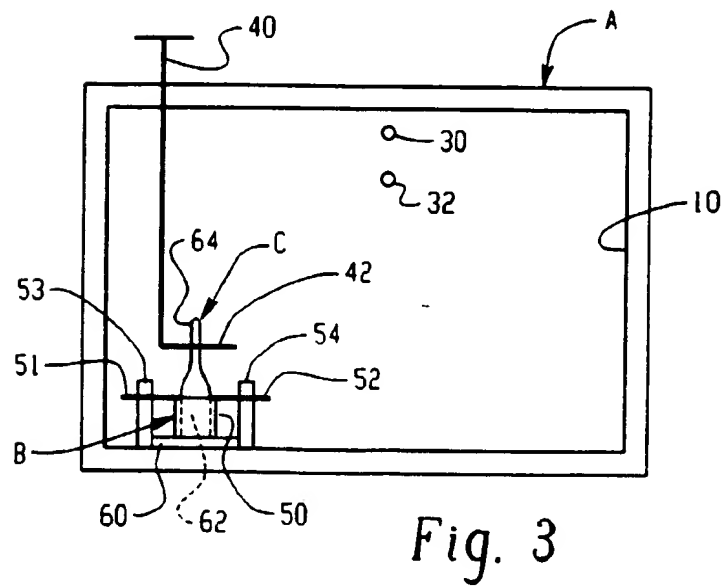
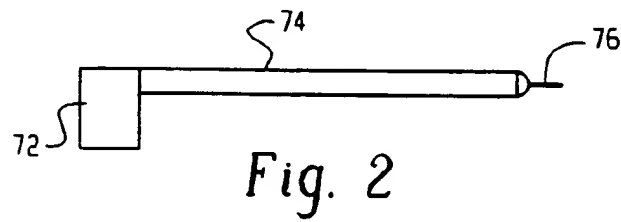
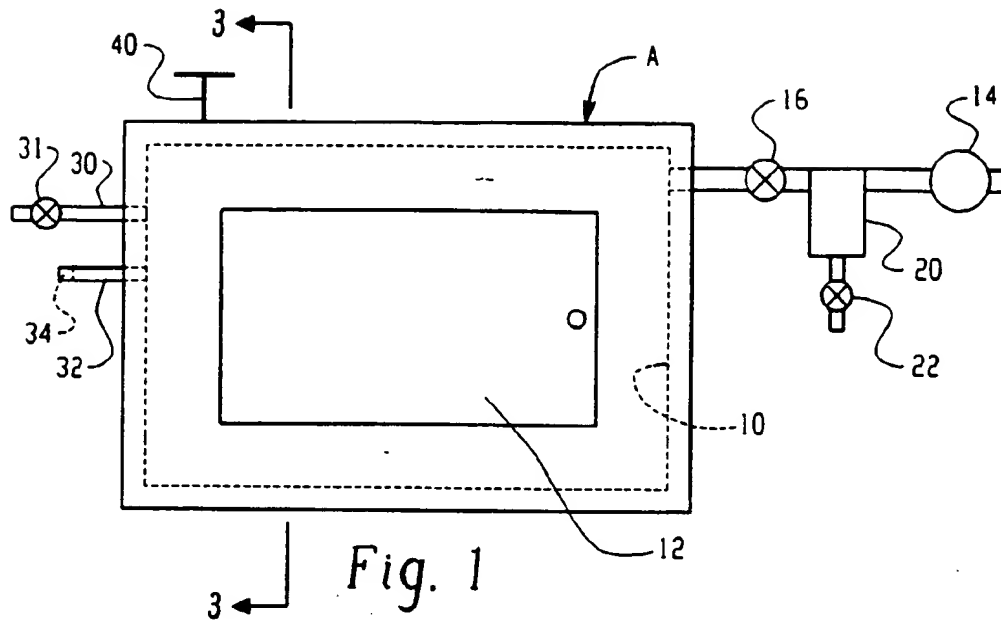
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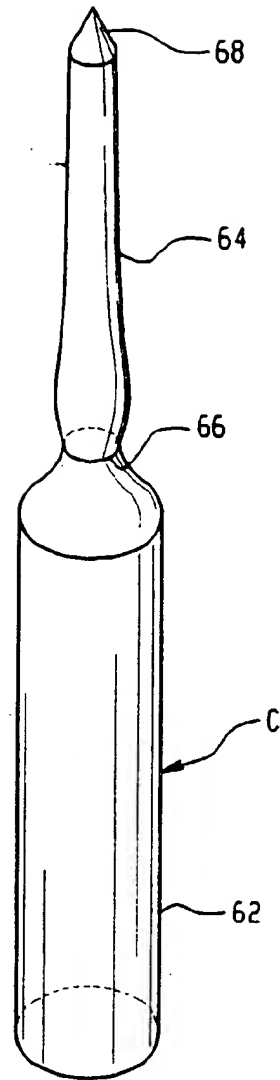


Fig. 4

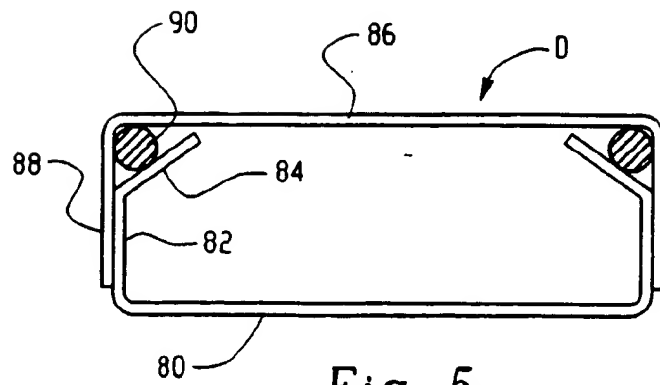
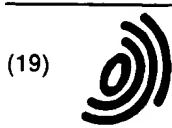


Fig. 5



(19)

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(11)

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(12)

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08.03.2000 Bulletin 2000/10

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C03C 17/30, C03C 17/00

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(30) Priority: **26.05.1998 US 84944**

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(54) Method for modifying surfaces with ultra thin films

(57) A substrate surface is coated with a thin film by exposing the substrate to a vapor of amphiphilic mole-

cules in a vacuum chamber (A), and allowing the amphiphilic molecules to spontaneously self-assemble and attach to the substrate surface.

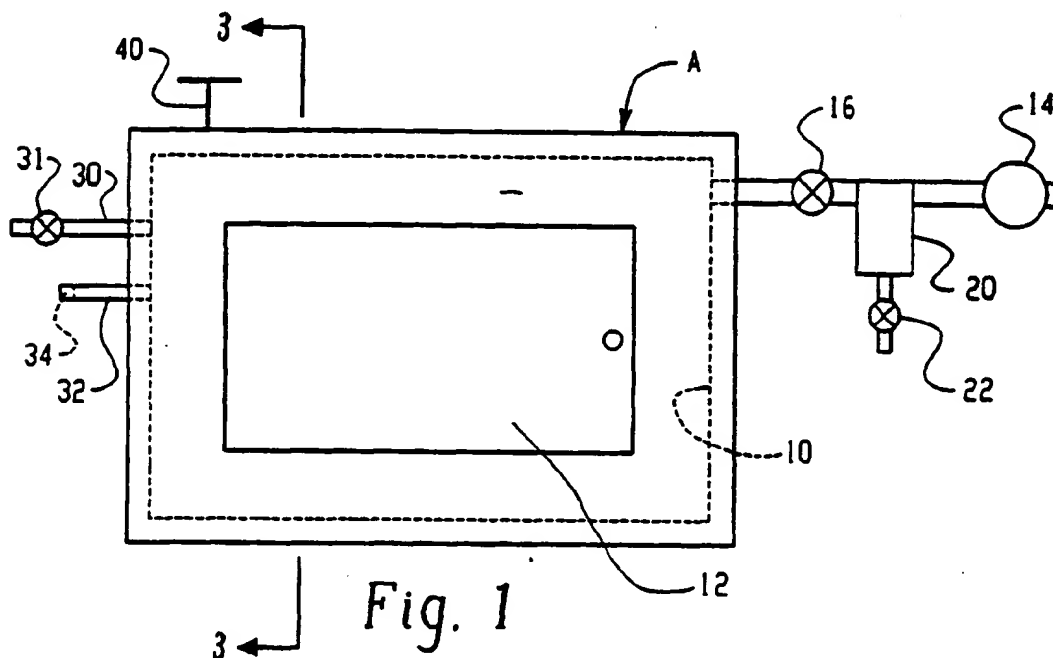


Fig. 1

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EUROPEAN SEARCH REPORT

Application Number
EP 99 30 4053

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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 10 January 2000	Examiner Reedijk, A
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03 82 (P04C01)



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Application Number

EP 99 30 4053

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ Only part of the claims have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid, namely claim(s):
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

see sheet B

- ☒ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ As all searchable claims could be searched without effort justifying an additional fee, the Search Division did not invite payment of any additional fee.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid, namely claims:
- ☐ None of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims, namely claims:



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**LACK OF UNITY OF INVENTION
SHEET B**

Application Number
EP 99 30 4053

The Search Division considers that the present European patent application does not comply with the requirements of unity of invention and relates to several inventions or groups of inventions, namely:

1. Claims: 1-15

method for modifying surfaces with ultra thin films

2. Claims: 16-18

container containing amphiphilic material

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 30 4053

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